

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-092119

(43)Date of publication of application : 06.04.1999

(51)Int.Cl.

C01B 13/34
C01G 45/00
H01M 4/02
H01M 4/58

(21)Application number : 09-270396

(71)Applicant : TOYOTA CENTRAL RES & DEV
LAB INC

(22)Date of filing : 16.09.1997

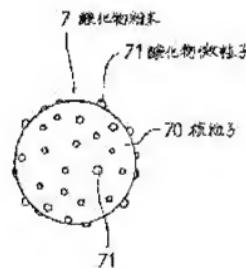
(72)Inventor : SASAKI ITSUKI
TAKATORI KAZUMASA
WATANABE NAOYOSHI
NORITAKE TATSUO
SUGIYAMA JUN
HATANAKA TATSUYA

(54) OXIDE POWDER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain oxide powder having characteristics of a plurality of oxides and capable of suppressing the formation of aggregates owing to the rugged surface shape.

SOLUTION: Nuclear particles 70 of an oxide are prep'd. and fine oxide particles 71 different from the nuclear particles 70 in compsn. are stuck to the surfaces of the nuclear particles 70 to obtain the objective oxide powder 7. The nuclear particles 70 may be particles of lithium manganese double oxide and the fine oxide particles 71 may be fine particles of LiMO_2 (M is a transition metal such as Co, Ni, Fe, Cr, Ti or V).



*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the special-shaped oxide powder which adheres particles to the surface.

[0002]

[Description of the Prior Art] Oxides, such as a metallic oxide and a metal multiple oxide, are used also as a positive electrode material of the lithium secondary battery for which it is used in various fields for example, which attracts attention these days. As a conventional positive electrode material for lithium secondary batteries, LiCoO_2 of regular arrangement stratified halite structure has been used. However, this thing is replacing the lithium manganese multiple oxide (LiMn_2O_4) of Spinel structure in that status from a point of resource quantity and a price.

[0003] this LiMn_2O_4 -- LiCoO_2 -- a ratio -- it has the fault that the diffusion rate of BE ** lithium is slow, and that conductivity is low. Therefore, capacity deterioration is [that it is hard to obtain big service capacity] also large when charge and discharge are performed with high current density. Therefore, ideally, the oxide powder having the strong point of both the above-mentioned LiMn_2O_4 and LiCoO_2 is desirable as a positive electrode material.

[0004]

[Problem(s) to be Solved] In order to solve the fault of the charging and discharging characteristic in the high current density of above LiMn_2O_4 , it is high crystallinity conventionally and powder with small particle diameter is proposed. For example, the atomized firing composition shown in JP,7-81905,A hits it. However, the characteristic which matches LiCoO_2 also in this improvement is not obtained.

[0005] The powder with small particle diameter has the fault that generally a filling factor does

not increase bulky. This is because the adhesion force between particles becomes large relatively to particle weight. The decline in a filling factor causes the fall of electrode density, i.e., the fall of cell capacity. The moldability at the time of using an electrode for the adhesion force between the particle has the fault that it is bad.

[0006]Then, these two SUBJECT, artificers;

(1) In order to solve the fall of the charge-and-discharge capacity in the high current density which conductivity is low or originates in lithium diffusion speed being slow, the decline in the filling factor resulting from the adhesion force between (2) particles, and the fall of the moldability at the time of electrode production, it inquired wholeheartedly. As a result, it considered arranging the oxide impalpable powder which has the characteristic which is different from this on the surface of the oxide particle used as a core to rugged form. If this is realized, the adhesion force between particles decreases by a concavo-convex effect, restoration nature and moldability can be raised and the oxide powder having the characteristic which was not obtained and was excellent in the independent oxide can be obtained.

[0007]In above LiMn_2O_4 , by arranging conductive oxide impalpable powder or oxide impalpable powder with an early diffusion rate of lithium, The decline in the filling factor which controls the fall of the charge-and-discharge capacity in the high current density which conductivity is low or originates in a RICHIMU diffusion rate being slow, and originates in the adhesion force between particles, and the fall of the moldability at the time of electrode production can also be suppressed.

[0008]This invention was made in view of this conventional problem, and has the characteristic of two or more oxides, and it tends to provide the oxide powder which the adhesion force between particles can reduce with surface uneven shape.

[0009]

[Means for Solving the Problem]This invention adheres oxide particles of a different presentation from this to the surface of a nuclear particle which consists of oxides, and is in oxide powder characterized by things.

[0010]Each particle from which what should be most observed in this invention constitutes the above-mentioned oxide powder adheres the above-mentioned oxide particles to the surface of the above-mentioned nuclear particle, and the above-mentioned nuclear particle and the above-mentioned oxide particles are comprising an oxide of a mutually different presentation.

[0011]As for particle diameter of the above-mentioned oxide particles, it is preferred to use the range of 1 / 5 - 1/100 of a size of a grade which adheres on the surface of a nuclear particle, i.e., particle diameter of a nuclear particle. When particle diameter of oxide particles exceeds a mentioned range, there is all a problem that clear uneven shape cannot be formed on the surface of a nuclear particle.

[0012]Next, it explains per operation of this invention. Oxide powder of this invention adheres

the above-mentioned oxide particles to the surface of the above-mentioned nuclear particle. Therefore, in a particle surface of the above-mentioned oxide powder, uneven shape is formed of an adhesion portion of the above-mentioned oxide particles, and an unadhered portion. The uneven shape of this particle surface can demonstrate an effect of reducing adhesion force of mutual particles, and can control formation of floc substantially. So, the oxide powder of this invention can raise substantially bulk density at the time of fabricating, for example to a green compact etc. Powdered mobility and moldability are also improved by reduction of adhesion force between particles.

[0013]The above-mentioned oxide powder is constituted by two different oxides of the above-mentioned nuclear particle and the above-mentioned oxide particles. Therefore, it has simultaneously the outstanding characteristic which a nuclear particle has, and the outstanding characteristic which oxide particles have. So, according to this invention, it has the characteristic of two or more oxides, and oxide powder which can control formation of floc with surface uneven shape can be provided.

[0014]Next, the above-mentioned nuclear particle is a lithium manganese multiple oxide, and the above-mentioned oxide particles can be made into LiMO_2 (transition metals, such as

$\text{M}=\text{Co}$, nickel, Fe, Cr, Ti, and V) represented by LiCoO_2 . Thereby, the above-mentioned oxide powder is applicable as an outstanding positive electrode material in a lithium secondary battery.

[0015]That is, oxide powder in this case is constituted after LiMO_2 represented by many LiCoO_2 has adhered to the surface of a nuclear particle of a lithium manganese multiple oxide. Therefore, conductivity which excelled [nuclear particles / cheap and resource-rich] in the above-mentioned oxide particles can be added. A filling factor in a case of forming an anode can be conventionally raised according to floc depressor effect of the above-mentioned uneven shape.

[0016]If this LiMO_2 is chargeable and dischargeable in the same voltage range as LiMn_2O_4 , the whole capacity will not decrease greatly. So, this oxide powder demonstrates high service capacity and outstanding effects, such as an increase in charge-and-discharge capacity in high current density, and an increase in charge-and-discharge capacity per volume, especially, when it applies to a positive electrode material of a lithium secondary battery.

[0017]Next, the account of the upper as a method of manufacturing outstanding oxide powder, Are the method of manufacturing oxide powder which adheres oxide particles of a different presentation from this to the surface of a nuclear particle which consists of oxides, and produce a raw material aqueous solution containing raw material ion of the above-mentioned oxide particles, and. Into this raw material aqueous solution, distribute the above-mentioned nuclear particle, subsequently to inside of a flammable liquid this raw material aqueous

solution is made to become turbid, an emulsion, and nothing and this emulsion are sprayed liquid drop-like, a flammable liquid in this drop is burned, and there is a manufacturing method of oxide powder compounding the above-mentioned oxide powder.

[0018]What should be most observed in this manufacturing method is making the above-mentioned raw material aqueous solution distribute the above-mentioned nuclear particle beforehand, and performing an atomized firing synthetic method using this raw material aqueous solution.

[0019]As the above-mentioned nuclear particle, what has the particle diameter of 0.5-5 micrometers is used. There is a problem that formation of uneven shape on the surface of a nuclear particle is difficult when particle diameter is less than 0.5 micrometer, and on the other hand, in exceeding 5 micrometers, there is a problem that operation of an atomized firing synthetic method is difficult. The above-mentioned nuclear particle is producible by various methods, such as the conventional atomized firing synthetic method and a solid reaction method, for example.

[0020]As the above-mentioned raw material aqueous solution, raw material ion of oxide particles, i.e., a material element of oxide particles made profitably like, is included by an ionic state. For example, when it deposits oxide particles of a lithium cobalt multiple oxide on the nuclear particle surface, the above-mentioned raw material aqueous solution is made to contain a lithium ion and cobalt ion.

[0021]The above-mentioned raw material aqueous solution is made to become turbid in a flammable liquid, and is made with an emulsion. A thing which does not contain kerosene, gas oil, a fuel oil, gasoline, etc. as a flammable liquid used at this time, and does not contain a metal ion as an emulsifier for emulsion formation, especially the Nonion system surface-active agent are desirable, and a glycerine fatty acid ester etc. are used.

[0022]Combustion flame temperature of an emulsion in a reactor at the time of atomized firing composition of the above-mentioned emulsion is set up according to a kind of oxide powder to compound. For example, when it deposits oxide particles of a lithium cobalt multiple oxide on the surface of a nuclear particle of a lithium manganese multiple oxide, it is preferred to consider it as 600-900 **. At less than 600 **, there is a problem in the stability of combustion. On the other hand, when it exceeds 900 **, there is a problem that a lithium manganese multiple oxide will decompose.

[0023]Next, it explains per operation of this invention. In this invention, the above-mentioned nuclear particle is beforehand distributed in the above-mentioned raw material aqueous solution, this raw material aqueous solution is further changed into the above-mentioned emulsion state, and atomized firing composition is performed. Therefore, oxide powder which adheres oxide powder of a presentation which is different on the surface of the above-mentioned nuclear particle can be manufactured easily.

[0024]That is, in this manufacturing method, an emulsion which made the above-mentioned raw material aqueous solution become turbid to abbreviated homogeneity in a flammable liquid is sprayed liquid drop-like. In a sprayed drop, a raw material aqueous solution of a size of abbreviated homogeneity contains in the state where it was wrapped in a flammable liquid. Furthermore into each raw material aqueous solution, it will be in the state where a nuclear particle distributed beforehand contained.

[0025]And a process of deliquoring, a pyrolysis, and crystal growth advances for every raw material aqueous solution from which each sprayed drop was wrapped in this by combustion of a flammable liquid. Specifically, the new oxide particles compounded from a raw material aqueous solution deposit and adhere to the surface of a nuclear particle which already exists in the state of an oxide.

[0026]Therefore, oxide powder obtained turns into oxide powder which has the uneven shape to which much oxide particles were made to adhere on the surface of a nuclear particle, and demonstrates an outstanding operation effect mentioned above. In this manufacturing method, not all particles obtained turn into particles of such a structure, but particles of an independent state of oxide particles or a nuclear particle may be contained.

[0027]Thus, according to this manufacturing method, it has the characteristic of two or more oxides, and a manufacturing method of oxide powder which can control formation of floc with surface uneven shape is obtained.

[0028]

[Embodiment of the Invention]

It explains using drawing 1- drawing 4 about oxide powder concerning the example of an embodiment of example of embodiment 1 this invention, and a manufacturing method for the same. In this example, as shown in drawing 1, with the atomized firing synthetic method concerning the manufacturing method of this invention. The oxide powder 7 which adheres the oxide particles 71 of the lithium cobalt multiple oxide which consists of a presentation of LiCoO_2 to the surface of the nuclear particle 70 of the lithium manganese multiple oxide which consists of a presentation of $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$ was manufactured (sample E1).

[0029]The powder (the sample C1, C2) of the lithium manganese multiple oxide which consists of a presentation of $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$, respectively with the conventional atomized firing synthetic method and two kinds of manufacturing methods of the conventional solid phase technique , was produced for comparison.

[0030]First, the outline of an atomized firing synthesizer unit is shown in drawing 2. This device consists of the metering pump 1 which supplies an emulsion, the atomizer 2 which sprays an emulsion, the pilot burner 3 for ignition, the combustion reaction tower 4 of cylindrical shape, and the collector 5 for particle recovery. And the above-mentioned metering pump 1 is

connected to the mixing tank 11 into which the emulsion 110 was put. The samples E1 and C1 were produced using this device. The sample E1 is an example of this invention, and the sample C1 is a comparative example.

[0031](Manufacture of the sample E1) The lithium nitrate (LiNO_3) as a source of a lithium ion, The solution which melted the cobalt nitrate ($\text{Co}(\text{NO}_3)_2$ and $6\text{H}_2\text{O}$) as a source of cobalt ion so that Li:Co might become a rate of 1:1 by a mole ratio was adjusted so that it might become [I.] in 0.05 mol /by cobalt ion concentration, and it was used as the raw material aqueous solution.

[0032]Subsequently, 48.9g added to the above-mentioned raw material aqueous solution, and it was made to mix and distribute per I. the oxide particles of a lithium manganese multiple oxide which have the particle diameter of about 1 micrometer. This particle is a thing of a presentation of $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$. Next, the raw material aqueous solution which distributed the above-mentioned oxide particles was made suspended in the kerosene as a flammable liquid which melted the glycerine fatty acid ester as an emulsifier, and the emulsion 110 was produced in the mixing tank 11.

[0033]Subsequently, it was made to spray liquid drop-like in the combustion reaction tower 4 by supplying this emulsion 110 to the atomizer 2 with the metering pump 1, and spraying oxygen gas from the surroundings. And *** of the mixed gas of hydrogen and oxygen was supplied from the pilot burner 3, by this, the flammable liquid in the above-mentioned emulsion was lit, and atomized firing composition was performed within the combustion reaction tower 4.

[0034]The flame temperature of the emulsion to which atomized firing composition is performed was about 900 **. Forcible supply of the air was carried out from the exterior to the reactor so that it might not become hypoxia at the time of combustion. The oxide powder compounded by combustion was collected in the collector 5. This was made into the sample E1.

[0035](Manufacture of the sample C1) The lithium nitrate (LiNO_3) as a source of a lithium ion, The solution which melted manganese nitrate 6 hydrate ($\text{Mn}(\text{NO}_3)_2$ and $6\text{H}_2\text{O}$) as a source of manganese ion so that Li:Mn might become a rate of 1.03:1.97 by a mole ratio was adjusted so that it might become [I.] in 1.97 mol /with manganese ion concentration, and it was used as the raw material aqueous solution. And it used as it is, without adding the above oxide particles to this raw material aqueous solution. Others produced the particles of the lithium manganese multiple oxide like the manufacturing method of the above-mentioned sample E1. This was made into the sample C1.

[0036](Manufacture of the sample C2) The sample C2 was manufactured with the conventional solid reaction method. Using the particles of lithium carbonate (Li_2CO_3) and manganese

dioxide (MnO_2) as a raw material, it mixed so that Li:Mn might be set to 1.03:1.97 by a mole ratio. Mixing was performed by the planetary ball mill by using ethanol as a solvent. After drying this mixed granule child, press forming was carried out to the pellet type, and it heat-treated in oxygen for 800 ** and 8 hours. This pellet was fully ground and the particles of the lithium manganese multiple oxide of $Li_{1.03}Mn_{1.97}O_4$ of the same presentation as the above were obtained. This was made into the sample C2.

[0037]Next, in this example, the particle shape of the three above-mentioned samples E1, C1, and C2 was evaluated by performing SEM observation. In order to evaluate the restoration nature of synthetic particles quantitatively, application-of-pressure bulk density was measured on condition of 10 g of samples, dice inside diameter phi30mm, and application-of-pressure 1ton.

[0038]The result of the above-mentioned SEM observation is shown in drawing 3 and drawing 4. Drawing 3 is a SEM photograph of the sample E1 by the example of this invention. Drawing 4 is a SEM photograph of the sample C1 by the conventional comparative example. All are 5000 times as many photographs. The particles of the sample E1 formed in the circumference of a nuclear particle the surface state of the uneven shape to which much oxide particles adhered so that it might be known from these figures.

[0039]On the other hand, although the particle diameter of the sample C1 was almost equivalent to the sample E1, there had been no uneven shape in the surface not much. As for this sample C1, the shape itself varies and many particles of distorted shape, such as burst particles, were seen. Although the SEM photograph is not shown about the particles of the sample C2, this has large particle diameter 1 ***** compared with the sample E1 and C1 as known conventionally.

[0040]Next, the measurement result of the above-mentioned application-of-pressure bulk density is shown in Table 1. As known in Table 1, it turns out that bulk density with the highest sample E1 was shown, and formation of the above-mentioned uneven shape has contributed to improvement in bulk density directly. The thing with low bulk density of the sample C1 is considered because there are many particles of distorted shape, such as an empty capsid.

[0041]

[Table 1]

(表1)

試料名	嵩密度 (g/cm ³)
E 1 (本発明品)	2. 9 5
C 1 (従来の噴霧燃焼合成法)	2. 4 6
C 2 (固相反応法)	2. 5 7

[0042]In the example of two examples of an embodiment, the lithium secondary battery was assembled, respectively, using three samples (E1, C1, C2) manufactured in the example 1 of an embodiment as a positive electrode material, and the characteristic was evaluated.

[0043]First, it explains per composition of the above-mentioned lithium secondary battery. In making the anode of the above-mentioned lithium secondary battery, the polyvinylidene fluoride (PVdF) which are 7wt% and a binder about the carbon which is 85wt% and a conducting agent about the oxide powder of above-mentioned sample E1,C 1,C2 first -- 8wt% - it used and wet blending was carried out to the positive electrode mixture paste by making these into N-methyl, 2, and the pyrrolidone (NMP) which is a solvent. Next, this positive electrode mixture paste was applied to aluminum foil by a thickness of 0.2 mm, was pressurized by after-desiccation 2.7 ton/cm², and the anode was produced.

[0044]On the other hand, one 0.4-mm-thick metal Li foil was used for the negative electrode. Between the above-mentioned anode and the negative electrode, the polypropylene nonwoven was interposed as a separator. A 1-N LiPF₆ solution was used for the electrolysis solution in the above-mentioned lithium secondary battery. The solvent of this electrolysis solution is 1:1 mixed liquor of ethylene carbonate and diethyl carbonate.

[0045]Next, evaluation of the characteristic of the above-mentioned lithium secondary battery did the charge and discharge test as follows in order to evaluate a cycle characteristic and high service capacity nature simultaneously. First, the charge condition of each lithium secondary battery was made into the conditions of performing constant potential charge on this voltage, after it charged according to the constant current of 1 mA/cm² and voltage reached 4.3V after that until it was set to 4.3V. The sum total of the above charging time was made into 4 hours.

[0046]The discharging condition of each lithium secondary battery performed constant current discharge, and when 3.5V was reached, it ended discharge. And the discharge current density of constant current discharge was changed every 3 cycles. As for one to 3 cycle, ten to 12 cycle made 1mA/cm² and seven to 9 cycle 2mA/cm², and was made into 4mA/cm², and, specifically, 13 to 15 cycle made again 0.5mA/cm² and four to 6 cycle 0.5 mA/cm².

[0047]The above-mentioned charge and discharge test result is shown in drawing 5. The figure took active material service capacity (mAh/g) for the number of charging and discharging cycles on the vertical axis along the horizontal axis. Each discharge current density was shown on each plotted data. From the figure, the high service capacity nature of each lithium secondary battery can be evaluated by comparing from the data constellation of one to 3 cycle to the data constellation of ten to 12 cycle. A cycle characteristic (endurance) can be evaluated by comparing the data constellation of one to 3 cycle with the data constellation of 13 to 15 cycle.

[0048]As a result, this invention and the sample E1 by the conventional atomized firing

synthetic method, and C1 showed the high service capacity nature and the cycle characteristic which excelled the sample C2 of the solid reaction method in each. about the high service capacity nature in $4mA/cm^2$, the performance which the sample E1 of this invention was markedly alike, and was superior to the sample C1 was shown.

[0049]It is thought that the reason for having demonstrated the performance superior to the sample E1 and the sample C2 according [C1] to a solid reaction method is based on the characteristic with the sufficient homogeneity of lithium manganese multiple oxide particles that particle diameter is small and that specific surface area is large. It is thought that the reason for having demonstrated the electrode performance in which the sample E1 which is an example of this invention excelled the sample C1 is because the bulk density improved effect by the above-mentioned uneven shape and the conductivity improved effect by $LiCoO_2$ of oxide particles were demonstrated.

[0050]

[Effect of the Invention]According to this invention, like ****, it has the characteristic of two or more oxides, and the oxide powder which can control formation of floc with surface uneven shape can be provided.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]Oxide powder which adheres oxide particles of a different presentation from this to the surface of a nuclear particle which consists of oxides, and is characterized by things.

[Translation done.]